LASER ENGRAVED,HIGH GAIN ANODE FOIL AND METHOD OF MAKING SAME

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BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention is directed to a method of producing an electrode for use in the manufacture of electrolytic capacitors and more particularly to a method of creating porous electrode foil for use in multiple electrode stack configuration electrolytic capacitors of the type used in implantable cardioverter defibrillators (ICDs).

Related Art

[0002] Compact, high voltage capacitors are utilized as energy storage reservoirs in many applications, including implantable medical devices. These capacitors are required to have a high energy density since it is desirable to minimize the overall size of the implanted device. This is particularly true of an implantable cardioverter defibrillator (ICD), also referred to as an implantable defibrillator, since the high voltage capacitors used to deliver the defibrillation pulse can occupy as much as one third of the ICD volume.

near ideal properties in terms of size and ability to withstand relatively high voltage. Conventionally, an electrolytic capacitor includes an etched aluminum foil anode, an aluminum foil or film cathode, and an interposed kraft paper or fabric gauze separator impregnated with a solvent-based liquid electrolyte. The electrolyte impregnated in the separator functions as the cathode in continuity with the cathode foil, while an oxide layer on the anode foil functions as the dielectric. The entire laminate is rolled up into the form of a substantially cylindrical body, or wound roll, that is held together with

adhesive tape and is encased, with the aid of suitable insulation, in an aluminum tube or canister. Connections to the anode and the cathode are made via tabs. Alternative flat constructions for aluminum electrolytic capacitors are also known, composing a planar, layered, stack structure of electrode materials with separators interposed therebetween.

joules, their size can be relatively large, and it is difficult to package them in a small implantable device. Currently available ICDs are relatively large (over 44 cubic centimeters (cc)), generally rectangular devices about 12-16 millimeters (mm) thick. A patient who has a device implanted may often be bothered by the presence of the large object in his or her pectoral region. Furthermore, the generally rectangular shape can in some instances lead to pocket erosion at the somewhat curved corners of the device. For the comfort of the patient, it is desirable to make smaller and more rounded ICDs. The size and configuration of the capacitors has been a major stumbling block in achieving this goal.

element, it is desirable to use capacitors with the greatest possible capacitance per unit volume. Since the capacitance of an electrolytic capacitor increases with the surface area of its electrodes, increasing the surface area of the aluminum anode foil results in increased capacitance per unit volume of the electrolytic capacitor. By electrolytically etching aluminum foils, an enlargement of a surface area of the foil will occur. As a result of this enlargement of the surface area, electrolytic capacitors, which are manufactured with the etched foils, can obtain a given capacity with a smaller volume than an electrolytic capacitor which utilizes a foil with an unetched surface.

[0006] In a conventional electrolytic etching process, surface area of the foil is increased by removing portions of the aluminum foil to create etch tunnels. The foil used for such etching is typically an etchable aluminum strip of high cubicity. High cubicity in the present context is where at least approximately

85% of crystalline aluminum structure is oriented in a normal position (i.e., a (1,0,0) orientation) relative to the surface of the foil. Such foils are well-known in the art and are readily available from commercial sources. While electrolytic capacitors having anodes and cathodes comprised of aluminum foil are most common, anode and cathode foils of other conventional metals such as titanium, tantalum, magnesium, niobium, zirconium and zinc are also used.

U.S. Patent No. 4,213,835 to Fickelscher discloses a method for [0007] electrolytically etching a recrystallized aluminum foil which allows manufacture of foils with exclusively pure cylindrical or cubical etching structures and tunnel densities greater than 10⁷/cm² with an avoidance of irregular pitting of the foil. The method consists of providing an etching bath containing chloride ions, positioning the foil in the bath and potentistatically etching the foil with a temporally constant anode potential. The preferred etching step occurs in two stages. In the first stage, the etching current density is set above the potential or current density which creates pitting of the aluminum. After an induction period of around 10 seconds, the etching tunnels grow autocatalytically at a rate of several µm/s with a pore diameter of approximately 0.2 µm in the crystal oriented direction (i.e., a (1,0,0) orientation relative to the surface of the foil). After approximately one minute of exclusive tunnel formation and in order to avoid the occurrence of coarse pitting, the etching current density is reduced. In the second stage, the current density is set below the current density which creates pitting of the aluminum, such that only pore or tunnel enlargement up to the desired value will occur. Thus, the etching time for the tunnel enlargement is relatively long in relation to the etching time for obtaining the tunnel structure in the foil.

[0008] U.S. Pat. No. 4,420,367 to Löcher discloses a similar method for etching aluminum foil for electrolytic capacitors. Electrolytic tunnel formation is carried out in a first etching stage, as described above. However, the further etching for tunnel enlargement is non-electrolytic, taking place chemically in one or several etching stages. The method is preferably carried

out in a halogen-free or chloride-free solution having nitrate ions, such as HNO₃ and/or Al(NO₃)₃.

[0009]

U.S. Pat. Nos. 4,474,657, 4,518,471 and 4,525,249 to Arora disclose the etching of aluminum electrolytic capacitor foil by passing the foil through an electrolyte bath. The preferred bath contains 3% hydrochloric acid and 1% aluminum as aluminum chloride. The etching is carried out under a direct current (DC) and at a temperature of 75EC. U.S. Patent No. 4,474,657 is limited to the above single step. U.S. Patent No. 4,518,471 adds a second step where the etched foil is treated in a similar bath with a lower current density and at a temperature of 80-82.5EC. U.S. Patent No. 4,525,249 adds a different second step, where the etched foil is treated in a bath of 8% nitric acid and 2.6% aluminum as a nitrate, at a temperature of 85EC.

[0010]

The ideal etching structure is a pure tunnel-like etching with defined and uniform tunnel diameters and without any undesirable pitting of the foil. As tunnel density (i.e., the number of tunnels per square centimeter) is increased, a corresponding enlargement of the overall surface area will occur. Larger surface area results in higher overall capacitance. However, high gain etching of valve metals for use as anodes in electrolytic capacitors tend to produce very brittle anode foil. Typically the higher the gain of the anode foil, the more brittle the foil. In particular, the brittleness of the foil and its capacitance are both proportional to the depth of the etching and the density of the etch pits, i.e., the number per unit area. Accordingly, the capacitance and thereby the energy density are limited by the brittleness of the formed foil. As the brittleness of the formed foil increases, cracks formed in the foil more easily propagate across the foil, resulting in broken anodes. Therefore, there is a need for an improved method for etching anode foil which reduces the propagation of cracks that lead to broken anodes.

SUMMARY OF THE INVENTION

- [0011] The present invention is directed to a method of creating porous electrode foil for use in multiple anode stack configuration electrolytic capacitors, in order to reduce the equivalent series resistance (ESR) of such multiple electrode stack configurations without sacrificing capacitance. An electrolytic capacitor incorporating the etched anode foil of the present invention can be used in an implantable cardioverter defibrillator (ICD).
- [0012] A first embodiment of the present invention is directed to a method of producing an electrode for a capacitor from a foil. The method comprises, first, applying a laser beam to portions of the foil to create a pattern on the foil and, second, etching the foil.
- [0013] In a second embodiment, the method comprises, first, etching the foil followed by applying a laser beam to a portion of the foil to create a pattern on the foil.
- the surface of the foil to form a pattern. The pattern is formed by heating the foil surface to a temperature at which melting occurs. Alternatively, the pattern is formed by heating the surface of the foil to a temperature at which an oxide layer forms on the surface. Patterns formed include, for example, regular patterns such as horizontal or vertical lines, a grid pattern, a crossed-grid pattern, a parallel wave pattern, an intersecting wave pattern, a labyrinth pattern, a staggered hole pattern, or alternatively an irregular pattern. Moving the foil or moving the laser beam controls the formation of the pattern. A computer-controlled machine controls the movement of the foil or laser.
- [0015] The formation of the pattern on the foil reduces or prevents etching of the foil on the patterned areas. The patterned areas of foil form when the laser melts the foil and the foil solidifies on cooling. Alternatively, the pattern forms on the foil when the laser beam heats the foil to form an oxide layer. The oxide layer can be any oxide of the foil, preferably aluminum oxide. The

aluminum oxide layer acts as a mask to reduce or prevent etching. The areas where the laser was not applied etch more heavily.

the foil, preferably electrochemically. The foils are etched in an electrochemical bath comprising an anode portion and a cathode portion. The foils are placed in the anode portion, which further comprises an anode electrolyte. The anode electrolyte promotes electrochemical etching and comprises an aqueous solution of an oxidizer or alternatively, an oxidizer and an acid. A charge source is connected to the anode portion and the cathode portion. The cathode portion is any inert metal, for example titanium, gold or platinum. A current is caused to flow between the anode and cathode portions and the charge flow is monitored on the anode. The etching is complete when the charge on the anode reaches a predetermined level.

The foil is further processed in a widening step and a finishing step. The anode foil is suitable for use in an electrolytic capacitor with a multiple anode stack or wound roll configuration, after forming a barrier oxide sufficiently thick to support the intended use voltage. The electrochemical etching step of the present invention produces a pore structure in the anode foil which is microscopic in pore diameter and spacing. The combination of etched and unetched areas on the foil maintains high gain and high strength. The high strength and ductility of the foil is maintained by the patterned unetched (or less etched) areas which stop the propagation of any cracks that may form in the heavily etched areas.

BRIEF DESCRIPTION OF THE DRAWINGS/FIGURES

- [0018] FIG. 1A is a flow diagram showing a method of producing an electrode with, first, applying a laser to a foil.
- [0019] FIG. 1B is a flow diagram showing a method of producing an electrode with, first, etching a foil.
- [0020] FIG. 2A is the design of a grid pattern used in laser engraving a foil.

- [0021] FIG. 2B is a photomicrograph of a foil that was laser engraved with the grid pattern showing the intersection of scribes.
- [0022] FIG. 3A is a photomicrograph of a foil that was laser engraved with a cross-grid pattern.
- [0023] FIG. 3B is a photomicrograph of an intersection of the scribes in FIG 2B.
- [0024] FIG. 4A is a design of a ripstop pattern used in laser engraving a foil.
- [0025] FIG. 4B is a design of a labyrinth pattern used in laser engraving a foil.
- [0026] FIG. 4C is a design of a staggered hole pattern used in laser engraving a foil.
- [0027] FIG. 5A is a photomicrograph of a foil that was laser engraved with a cross-grid pattern with additional engraving at the intersections.
- [0028] FIG. 5B is a photomicrograph of a foil that was laser engraved with a grid pattern with additional engraving at the intersections and the center of each square in the grid.
- [0029] FIG. 6A is a photomicrograph of an unetched foil that was laser engraved with a staggered hole pattern with scribes connecting the holes.
- [0030] FIG. 6B is a photomicrograph of an etched foil that was laser engraved with a staggered hole pattern with scribes connecting the holes.
- [0031] FIG. 7 is a mask of the parallel wave pattern for computerized etching of foil sheets according to the invention.
- [0032] FIG. 8A is an of a finished anode foil that was engraved with a parallel wave pattern running across the aluminum foil grain.
- [0033] FIG. 8B is an of a finished anode foil that was engraved with an intersecting wave pattern.

DETAILED DESCRIPTION OF THE INVENTION

[0034] The first embodiment of the present invention is directed to a method of producing an electrode for a capacitor from a foil. As shown in FIG. 1A, the method comprises first applying a laser beam to the foil to create a regular

pattern on the foil surface and then by etching the foil. Alternatively, the method comprises creating an irregular pattern on the foil surface with the laser beam and then etching the foil. After etching, the foil is further processed in forming and finishing steps, or alternatively, in a finishing step.

laser beam to the foil to create a regular pattern on the foil surface. Alternatively, the method comprises creating an irregular pattern on the foil surface with the laser beam after etching the foil. As shown in FIG.1B, the step of applying the laser to the foil or alternatively the step of forming the foil is performed after the etching step. The forming step follows the step of applying the laser, or alternatively, the step of applying the laser follows the forming step. The foil is further processed in a finishing step.

[0036] The foil is made from any electrically conductive material. In the present invention, the foil is used as an electrode in a capacitor as an anode or alternatively as a cathode. Anode and cathode foils are made of metal, metal alloy, or a metal composite material, for example aluminum. Alternative materials include but are not limited to zinc, zirconium, tantalum, magnesium, niobium, and alloys of any or all of these metals.

The laser is applied to one surface of the foil. Alternatively, the laser or a combination of lasers is applied to one or both surfaces of the foil. The laser is applied to the foil surface to locally heat the metal foil to a temperature at which surface melting occurs. Removing the laser from the foil allows the foil to cool and solidify. Solidify is used herein to mean the transition in the physical state of the foil from a melted liquid to a solid as the foil cools. The final solid state can be either crystalline, amorphous or a mixture of the two. Alternatively, the laser is applied to the foil surface to locally heat the metal foil to a temperature that causes an oxide layer to form.

[0038] Lasers that are used in the present invention include lasers that cause local heating when applied to the foil surface, for example the Nd:VO₄ laser. Alternative lasers include but are not limited to Nd:YAG, He:Ne, CO₂, Argon ion, semiconductor, and organic or inorganic dye lasers. The laser is applied to

the foil surface for a time sufficient to cause melting or oxide formation and depends on the power and type of laser used. The spot size of the laser determines the width of the scribe. Scribe is used herein to mean the mark on the foil produced by the application of the laser to the surface of the foil. For example, the mark is a line, a series of lines, a dot, a series of dots, or any other geometric shape. The spot size of the laser is in the range from about 0.5 µm to about 50 µm, preferably from about 5 µm to about 25 µm.

[0039] The laser is applied to the foil in a predetermined regular pattern, or alternatively in an irregular pattern. Moving the foil while holding the laser substantially stationary, or alternatively, moving the laser while holding the foil substantially stationary forms the predetermined pattern. A computer-controlled machine controls the movement of the foil or laser. The invention allows for the production of detailed patterns of melted areas on the foil that solidify upon cooling, or alternatively detailed patterns of oxide on the surface of the foil. Computerized etching is performed by programming an etch pattern into a computer and the foil is etched according to the digital pattern. Alternatively, a patterned mask is applied to the foil sheet. The foil sheet is then etched using a computer controlled laser or by a hand controlled laser according to the pattern on the mask, which is applied to the foil sheet.

[0040] The patterns engraved on the foil can be any pattern, which includes, but is not limited to any regular, irregular or random pattern. For example, a series of horizontal, vertical, diagonal or circular lines are engraved across a foil. FIG. 2A illustrates a design for a grid pattern. FIG. 2B shows an intersection of two lines engraved on a foil in the grid pattern of FIG. 2A. FIG. 3A shows a foil that has been engraved with a crossed-grid pattern. FIG. 3B shows an intersection of the crossed lines in the crossed-grid pattern of FIG. 3A. FIG. 4A illustrates a design for a pattern of a series of vertical lines across a foil. FIG. 4B illustrates a design for a labyrinth pattern. FIG. 4C illustrates a design for a pattern having staggered engravings. FIG. 5A illustrates a crossed-grid pattern with additional engraving at select intersections. FIG. 5B shows a crossed grid pattern with additional engraving at select intersections

and at the center of each square in the grid. FIGS. 6A and 6B show a staggered-hole pattern with scribes connecting the holes. FIG. 7 shows a mask that is applied to a foil sheet for etching a parallel wave pattern into a foil sheet. FIG. 8A shows an example of a parallel wave pattern engraved on a finished anode. FIG. 8B shows an intersecting wave pattern engraved on a finished anode. Alternatively, a foil is engraved with a combination of patterns. A pattern is applied to one side of the foil. Alternatively, the pattern is applied to both sides of the foil or different patterns are applied to different sides of the foil.

Etching the foil increases the surface area of the foil. The foil is etched according to any method that increases the surface area, preferably electrochemical etching. Other methods include roughing the foil surface mechanically and chemical etching. Electrochemical etching increases the surface area of the foil by electrochemically removing portions of the foil to creates etch tunnels. Electrochemical etching is done according to any known etch process, such as the ones discussed in U.S. Patent Nos. 4,474,657; 4,518,471; 4,525,249 and 5,715,133 which are incorporated herein by reference.

etching. The electrolyte comprises a halide and/or oxyhalide, preferably a chloride and/or oxychloride, and an oxidizer such as hydrogen peroxide, sodium perchlorate, sodium persulfate, cerium sulfate or sodium periodate. The pH of the electrolyte is maintained in the range of about 0.0 to about 8.0, preferably a pH of about 1.0 to about 3.0. An acid is added to the electrolyte to maintain the pH, for example hydrochloric acid. Alternative acids for use in the present invention include but are not limited to sulfuric, nitric, hydrobromic, and hydrofluoric acids; or organic acids such as formic, acetic, citric and para-toluenesulfonic acid. Other surface area enhancing etch solutions can be used with the present invention to produce similar results. Preferably, the electrolyte etch solution comprises about 1.3 % by weight NaCl and about 3.5 % by weight NaClO4. The electrolyte is heated to a

temperature of about 80°C to about 100°C, with a preferred temperature of about 85°C. The foil is placed in the etch electrolyte and etched at a current density of about 0.1 to about 0.3 Amps/cm², preferably about 0.15 Amps/cm². The current density corresponds to an etch charge of about 5 to about 50 Coulombs/cm² for a specific amount of time, preferably about 36 Coulombs/cm² for about 4 minutes. The foil is etched to produce an enlargement of surface area of at least about 20 times.

In the first embodiment, a laser beam is applied to the foil surface to create a regular or irregular pattern and the foil is then etched. The laser melts a portion of the foil or alternatively causes an oxide layer to form on the foil surface. Upon etching, the areas where the laser was applied etch more slowly or not at all. The oxide layer acts as a mask between the foil surface and the etch electrolyte to retard or prevent etching. The areas where the laser was not applied etch more heavily. The patterned areas, in which little or no etching occurs, stop the propagation of cracks through the heavily etched portions. This pre-etch laser beam patterning increases the foil strength and ductility while allowing for relatively heavy foil etching, which gives high gain, high strength electrodes for ICD capacitors.

In the second embodiment of the invention, a foil is first etched and then the laser beam is applied to the foil surface. The entire are of the foil is first etched. A regular or irregular pattern is then applied to the foil using the laser beam. The pattern in the foil forms areas of strength where the propagation of cracks terminates. This post-etch laser beam patterning increases the foil strength and ductility while allowing for relatively heavy foil etching, which gives high gain, high strength electrodes for ICD capacitors.

In the first embodiment after the foil is etched, the foil is widened in a chloride or nitrate containing electrolyte solution known to those skilled in the art, such as that disclosed in U.S. Patent Nos. 3,779,877 and 4,525,249, which are incorporated herein by reference. The foil is then dipped into a deionized water bath at a temperature of 80EC to 100EC, preferably 95EC, to form a hydrate on the foil surface.

[0046] In the second embodiment of the invention, the laser beam is applied to the foil before widening. Alternatively, the laser beam is applied after widening the foil.

Next, a barrier oxide layer may be electrochemically formed onto one or both surfaces of the metal foil, sufficiently thick to support the intended use voltage, by placing the foil into a forming solution, including but not restricted to a solution based on azelaic acid, sebacic acid, suberic acid, adipic acid, dodecanedioic acid, citric acid or other related organic acids and salts. Preferably a citric acid is used solution at a temperature of about 80EC to 100EC, preferably 85EC, at a current density of about 1 mA/cm² to 40 mA/cm², preferably 16 mA/cm². A formation voltage of about 50 to 800 Volts, preferably 445 V, can be applied to the foil to form the barrier oxide layer. The barrier oxide layer provides a high resistance to current passing between the electrolyte and the metal foils, also referred to as the leakage current. A high leakage current can result in poor performance and reliability of an electrolytic capacitor. In particular, a high leakage current results in a greater amount of charge leaking out of the capacitor once it has been charged.

[0048] A heat treatment of about 500EC ± 20EC may be applied to the foil following formation for about 1 to about 10 minutes, preferably about 4 minutes. The foil is then returned to the forming solution and allowed to soak with no applied potential for about 1 to about 10 minutes, preferably about 2 minutes. A second formation in the same electrolytic forming solution at high temperature is performed at a potential of about 435 Volts.

[0049] Next, the foils are dipped in a suitable low concentration oxide-dissolving acid solution including but not restricted to phosphoric acid, formic acid, acetic acid, citric acid, oxalic acid, and acids of the halides. Preferably phosphoric acid is used at a concentration of about 1 % to 10 %, preferably a concentration of about 2 %, at a temperature of about 60EC to 90EC, preferably about 70EC, for an time of about one to about ten minutes, preferably about four minutes.

[0050] Finally, the foils are reformed at a voltage of about 435 Volts in a suitable forming solution, as discussed above, at a high temperature, preferably about 80EC to about 100EC, more preferably about 85EC.

[0051] Electrolytic capacitors manufactured with anode foils etched according to the present invention may be utilized in ICDs, such as those described in U.S. Patent No. 5,522,851 to Fayram, incorporated herein by reference. The increased capacitance per unit volume of the electrolytic capacitor will allow for a reduction in the size of the ICD.

[0052] The following examples are illustrative, but not limiting, of the method of the present invention. Modifications and adaptations of the parameters of the invention in response to issues normally encountered in manufacturing will be apparent to those skilled in the art and are within the spirit and scope of the invention.

EXAMPLE 1

[0053] A pattern was applied to a series of aluminum foils comprising about 97% high cubicity recrystallized aluminum. A Nd:YAG laser was used at about 45 Watts of power, a pulse frequency of about 4 kilohertz, a scan speed of about 41 mm/sec and a spot size of about 20 μm. FIG. 2A shows the design for the grid pattern. The line spacing is about 0.200 inches by about 0.200 inches. As shown in the photomicrograph of FIG. 2B, the application of the laser beam to the foil in the grid pattern formed distinct patterned areas of strength. The photomicrograph in FIG. 2B is of an intersection of the scribes created by the laser beam.

[0054] Using similar conditions, as shown in FIG. 3A, a crossed-grid pattern was applied to a foil. The crossed-squares have dimensions of 0.100 inches by 0.100 inches. FIG. 3B is a photomicrograph of an intersection of the crossed grid pattern.

[0055] The patterns in FIG. 5A and FIG. 5B were formed using a Nd:YAG laser at a scan speed of 380 mm/sec with a repetition rate of 8 kilohertz. FIG.

5A is a photomicrograph of a crossed-grid pattern with staggered holes and additional engraving at the intersections. FIG. 5B is a photomicrograph of a grid pattern with staggered holes and additional engraving at the intersections and additional engraving at the centers of the squares in the grid.

EXAMPLE 2

[0056] A Nd:YAG laser operating at 45W and 13.13 kilohertz was used to apply a pattern on four aluminum foils, comprising at least about 97% cubic structure aluminum, at a scan speed of 375 mm/sec. The pattern is a staggered hole array with connecting lines that form squares with dimension of 0.100 inches by 0.100 inches. The laser is applied to four foils. Two of the foils are etched after the laser application. FIG. 6A is a photomicrograph of an unetched foil and FIG. 6B is a photomicrograph of an etched foil. The mean capacitance of the etched foils is 342.92 μF/cm², while the mean capacitance of the unetched foils is 339.26μF/cm².

EXAMPLE 3

[0057] A Nd:YAG laser operating at 45W and 25 kilohertz was used to apply a pattern on sixteen aluminum foils, comprising at least about 97% cubic structure aluminum, at a scan speed of about 448 mm/sec. The pattern is a parallel wave, applied across the grain of the aluminum. FIG. 8A is an image of an anode prepared with this pattern. The laser is applied to a 4.1 inch by 3.9 inch foil in 50 seconds. Sixteen control foils are etched without applying a laser beam to the foil surfaces. The capacitance is measured for the patterned foils and the control foils. The mean capacitance for the patterned foils is 331.75 μF/cm² and 347.81 μF/cm² for the control foils. The standard deviation in the patterned foils is 10.036 for the patterned foils and 19.95 for the control foils.

EXAMPLE 4

- [0058] Punch yields were calculated on sixteen foils, each comprising at least about 97% cubic structure aluminum. A Nd:YAG laser operating at 45W and 20 kilohertz was used to apply an intersecting wave pattern at a scan speed of 375 mm/sec. FIG. 8B is an image of one example of the finished anode. Foils produced from about 17 to about 24 anodes with a mean of 21.25, a 88.5% yield with standard deviation of 1.949359.
- [0059] While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and the scope of the invention.